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(54) Title: BETAKETOSULFONIC DERIVATIVES SUITABLE TO THE USE AS POLYMERIZATION PHOTOINITIATORS AND PHOTOPOLYMERIZABLE SYSTEMS CONTAINING THE SAME

(57) Abstract

New betaketosulfonic derivatives, the process for their preparation, the photopolymerizable systems containing the same and their application as polymerization photoinitiators for inks, and particularly for inks having high content of pigments are described.

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BETAKETOSULFONIC DERIVATIVES SUITABLE TO THE USE AS POLYMERIZATION PHOTOINITIATORS AND PHOTOPOLYMERIZABLE SYSTEMS CONTAINING THE SAME

FIELD OF THE INVENTION

The present invention concerns new betaketosulfonic derivatives suitable to the use as polymerization photoinitiators. the process for their praparation and the photopolymerizable systems containing the same.

Said systems find application in the inks field and particularly in the field of the inks having high content in pigments.

PRIOR ART

The photochemical polymerization of monomers and unsaturated prepolymers is a widespread technique used in various technological fields. such as those of paints and lacquers. of printing inks. in the making of printing plates and electronic circuits. stencils for ceramics and textile printing. and in the manufacture of dental apparatuses.

In particular. in the production of printing inks. the used photocross linkable systems are based on active monomers. such as derivatives of the acrylic and methacrylic acid. N-vinylpyrrolidone. vinyl ethers. styrene. allyl derivatives. maleic and fumaric acid derivatives; on ethylenic unsaturated polyester. polyether. polyurethane. silicone. epoxy oligomers and polymers; on pigments. fillers. additives. various auxiliares. on a photoinitiator or on a system composed of a mixture of photoinitiators. some of them particularly suitable to the pigmented system and other acting as adjuvants (benzophenone. benzyldimethylketale etc.). The constituent parts of these systems of

photoinitiators are generally:

a) a photoinitiator at least, which must show an absorption spectrum in the spectral region where resins and pigments have a minimum in absorpion or reflection of the incident light (optical window) and where the light source used for the process emits a peak or a radiation band (light).

For the photoinitiator systems at present in use, this region is located between 360 and 420 nm.

b) a coinitiator at least, generally a tertiary amine with hydrogen atoms available on carbon in alpha position with respect to nitrogen, which is essential when the photoinitiator acts by a hydrogen extraction mechanism, such as benzophenone and thioxanthones.

Said coinitiator in any case turns out to be very useful even in the case of photoinitiators acting by homolytic breaking: in fact the tertiary amines eliminate the oxygen inhibitory effect, increasing the speed of the whole photopolymerization process.

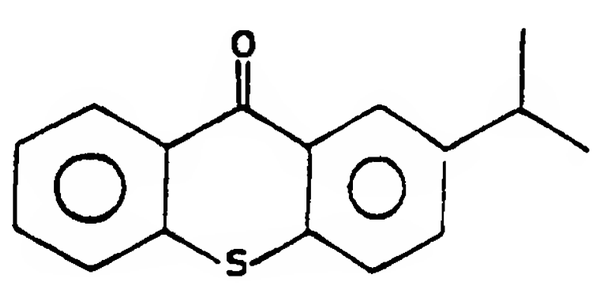
The polymerization inhibition owing to oxygen is a problem particularly important for printing inks, considering their limited thickness and their high surface/volume ratio.

For such purposes aromatic aliphatic or entirely aliphatic amines are generally used, such as for instance triethylamine, N-methyldiethanolamine, N,N-dimethylethanolamine, p-dimethylaminoethylbenzoate, as is for instance described in the Patent US 4 318 791.

The photopolymerization of pigmented printing inks has always shown various technical problems connected to the existence of some necessities:

- attainment of drying rates lying in the 15-200 m/min range, compatible with the industrial application in printing and graphic arts;
- achievement of a perfectly cross-linked film, avoiding the variation of the tone of the pigments added to the system, such as an undesired yellowing of the obtained film;
- perfect covering of the support, to obtain which a high pigmentation is needed, about 20-60% by weight;
- safety in the working environment limiting the residual odour, due to photolysis products or to not reacted monomers, particularly to acrylates, and limiting the presence of volatile substances during the photopolymerization stages.

Among the photoinitiators which have found grater use in the ink field there is the isopropyl thioxanthone (ITX), having the following formula



and similar derivatives (for instance the diethyl thioxanthone), as described in the American Patent US 4 434 035.

However the compound has the drawback to be coloured and consequently to give an undesired colouring to the white or light tone inks.

Some attempts to correct such defects have been carried out, as described in the European Patent EP 88050, with the introduction of the photoinitiators belonging to the class of the aminoketones, among which the 2-methyl-1-[4-(methylthio)phenyl] -2-morpholino -1-propanone

(MMMP) has been developed.

In this case the yellowing of the film turns out to be very low, but a serious limitation is presented by the residual odour due to the photolysis by-products of the photoinitiator after the irradiation process. Such odour is the cause of drawbacks during the productions in the working environment and persists in the processed goods; therefore the use of this product cannot be enlarged to the printing of the packagings destined to the food industry.

The introduction of such products on the market has been therefore limited and at the present time the coexistence of ITX and MMMP is noticed.

Recently the Applicant himself discovered a new family of photoinitiators of betaketosulfonic kind, described in the patent US 5 026 740.

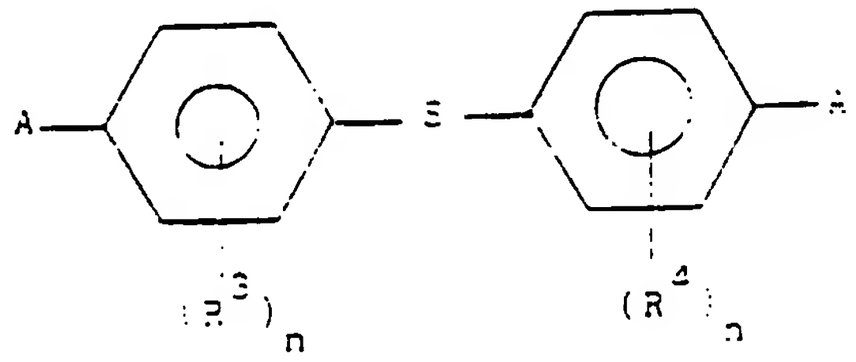
Some of the products belonging to such a class point out spectral requirements and reactivity suitable to the cross-linking of pigmented inks. The use of such compounds allow to obtain inks with a low yellowing degree, whether immediately after the exposure to the light sources, or by aging in the natural light; however the residual odour, even though not so marked as the previously cited cases, is a limit to their employment. Therefore the necessity is felt to find some products using which such residual odour after the photocross-linking is totally removed or remarkably reduced.

Within the limits of the family of photoinitiators just described, some structures have been surprisingly discovered showing photoinitiating properties, without generation of residual odour after the irradiation process, or generation of anomalous colouring or

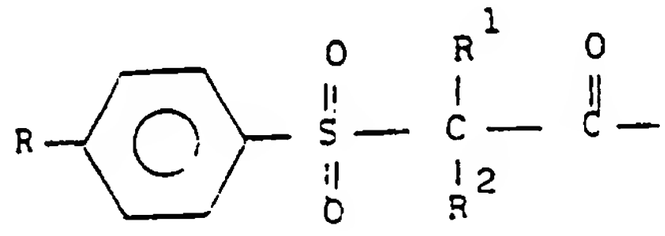
variation of tone of the film.

SUMMARY OF THE INVENTION

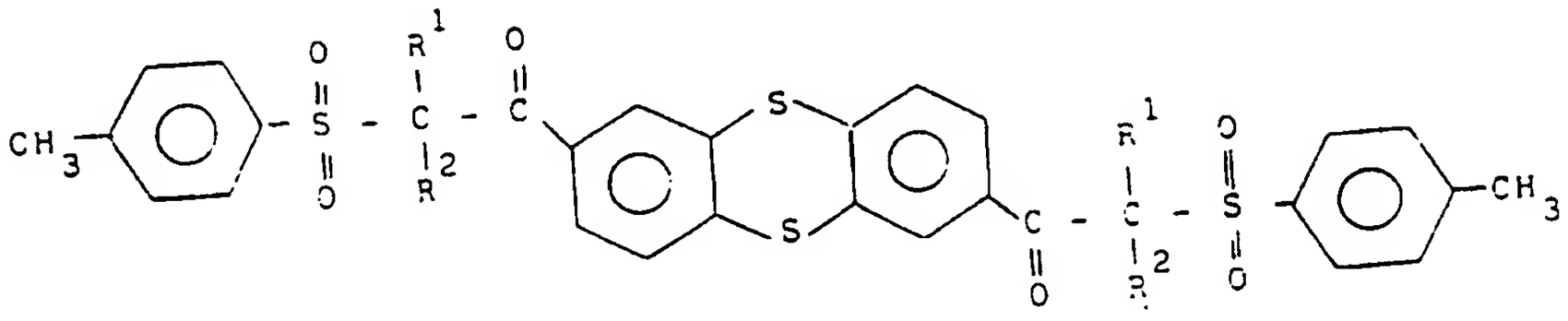
The present invention concerns photopolymerizable systems containing at least one betaketosulfonic derivative selected from the compounds having formula I:



wherein A is



and II:



wherein

R, R^1, R^2, R^3, R^4 each independently are H or C_{1-4} linear or branched alkyl chain and n is 0 or 1 particularly when said systems are pigmented inks.

Example of formula (I) is represented by the 4-4'-bis[2(4-methylphenylsulfonyl)-2-methyl-1-propanoyl]diphenyl sulfide, while an example of formula (II) corresponds to the 2,2-bis[2(4-methylphenylsulfonyl)-2-methyl-1-propanoyl]thianthrene.

The invention concerns, besides the compounds (I) and (II), the process for their preparation.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, the compounds having formula (I) and (II) are used as photoinitiators in photopolymerizable systems, containing reactive monomers and oligomers. The word "photopolymerizable system" means in the present text a mixture of photopolymerizable or cross-linkable monomers and oligomers, at least one photoinitiator, fillers, pigments, dispersants and other additives of general use. The expression "photopolymerization" is meant in broad sense and includes, for instance, also the further polymerization or cross-linking of polymeric material, for instance of prepolymers, the homopolymerization, and the copolymerization of simple monomers, and the combination of these kinds of reaction. The monomers suitable for the system of the present invention comprise the esters of the acrylic and methacrylic acid with aliphatic alcohols, glycols, polyhydroxylated compounds such as pentaerythritol or trimethylolpropane or aminoalcohols; acrylonitrile: acrylamide and their derivatives; esters of vinyl alcohol with aliphatic or acrylic

acids; vinyl ethers; N-vinylpyrrolidone; mono and polyfunctional allyl ethers such as the trimethylolpropandiallyl ether; styrene and alpha-methylstyrene; derivatives of maleic and fumaric acids.

The reactive oligomers suitable for the present invention include polyesters, polyacrylates, polyurethanes, epoxy resins, polyethers containing acrylic, fumaric or maleic functionality. The pigments used comprise inorganic pigments such as the titanium dioxide and the "Carbon Black", organic pigments on azo, phtalocyanine, anthraquinone etc. base.

The compounds (I) and (II) of the present invention act as photoinitiators and besides they may be used by themselves or in combination with other photoinitiators such as benzophenone, benzyldimethylketale, 2-hydroxypropylphenylketone, benzoin ethers etc. Particularly advantageous turns out the combination with tertiary amines which increase the cross-linking speed of the mixture, such as triethylamine, N-methyldiethanolamine, N,N-dimethylethanolamine, p-dimethylaminoethylbenzoate, in the way they are commonly used. For the pigmented systems turns out particularly advantageous the use of sensitizing substances or coinitiators, such as thioxanthones and their derivatives, in the way they are normally used.

In addition to the compounds having formula (I) and (II), many components may be included in the photopolymerizable system, such as thermal stabilizers, inhibitors of the thermal polymerization, sensitizers, photo-oxidations stabilizers such as steric hindrance amines, antioxidants, atmospheric oxygen exclusion agents, thermal generators of radicals such as organic and inorganic peroxides, peresters, hydroperoxides, benzopinacols, azoderivatives such as

azobisisobutyronitrile, metallic compounds such as cobalt (II) salts, manganese, surface levelling agents, fillers, dyes, glass and carbon fibers, thixotropic agents. Other components are constituted by unphotopolymerizable polymers, present as chemically inert substances, such as nitrocellulose, polyacrylic esters, polyolefines etc., or cross-linkable polymers by alternative systems such as peroxides and atmospheric oxygen, or by acid catalisys or thermal activation, such as for instance polyisocyanates, urea, melamine or epoxy resins.

Such photopolymerizable systems may be either of transparent kind or pigmented, and they are used in the printing, graphic arts, plastic meterials, metals, wood, glass etc. fields. Their use in the inks field, above all those having high pigmentation level must be particularly underlined: in this case the pigments are present in an amount ranging from 10 to 60% by weight, and preferably between 15 and 40% .

The compounds having formula (I) and (II) are generally used in a quantity between 0.01% and 20% by weight, and preferably between 0.5% and 5%; they show a great dispersibility in the photopolymerizable systems, to which they give a high photochemical reactivity and stability to light. The light sources used for the photopolymerization are high, medium or low-pressure mercury-vapor lamps or superactinic lamps, with emission bands in the region between 250 and 400 nm.

Among the possible sources even the sunlight or other artificial sources, such as xenon, tungsten lamps and laser sources are included.

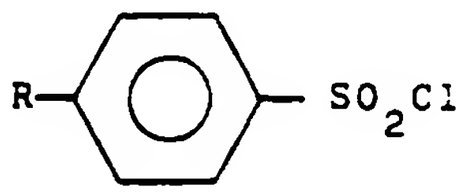
In the cross-linking of the inks containing titanium dioxide, "doped" lamps with a particularly high emission between 350 and 450 nm are preferably used.

In the inks preparation, the above mentioned compositions are ground on a three cilinders refiner till a granulometry between 0.1 and 2 µm and preferably lower than 1 µm is achieved. Such grinding may be carried out either formerly or subsequently to the addition by simple agitation of a photoinitiator and coinitiator mixture, wherein the photoinitiator is contained in an amount between 30 and 70%. Finally the polymerization is obtained by known methods, by irradiation in the suitable wavelength range.

In the preparation of the photoinitiators above shown, having formula (I) and (II), the use of many methods known in literature is possible. The process of sulfonylation of the respective halogenoketones, by the reaction of the halogenoketon with the sodium salt of the 4-alkylphenyl-sulfinic acid has been found particularly suitable.

Generally the process consists of the following steps:

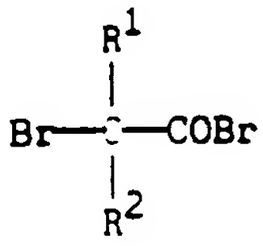
a) the arylsulfonyl chloride of formula (III) is made to react with sodium bicarbonate and sodium sulfite at a temperature between 50 and 90 °C, in a polar solvent, to give the corresponding sodium arylsulfinate:



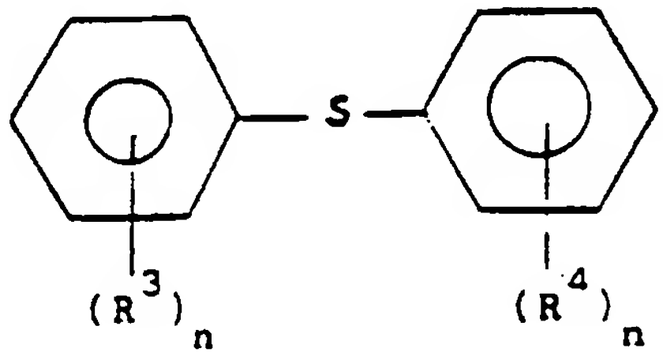
(III)

b) the dialkylbromoacetyl bromide of formula (IV) is made to react with the appropriate diphenyl sulfide of formula (V) (for the compounds (I) or with thianthrene (for compounds (II)), in presence of

aluminum trichloride, in an organic solvent, at a temperature between 5 and 15°C. and the mixture is treated with mineral acids to give the corresponding 2-bromoketones for instance 4,4'-bis(2-bromo-2-methyl-1-propanoyl)-diphenyl sulfide (for the compounds (I)) or 2,6-bis(2-bromo-2-methyl-1-propanoyl)thianthrene (for the compounds (II));



(IV)



(V)

c) a mixture of sodium arylsufinate obtained in the step a) and the appropriate 2-bromoketone for instance 4,4'bis(2-bromo-2-methyl-1-propanoyl)-diphenyl sulfide (for the compounds (I)) or 2,2-bis(2-bromo-2-methyl-1-propanoyl)thianthrene (for the compounds (II)), obtained by the step b), at a temperature between 80 and 120 °C in an organic solvent, is heated to give the final products (I) and (II).

The following examples of the present invention are reported for illustrative but not limitative aim:

EXAMPLE 1

Synthesis of the photoinitiator having formula (I): wherein n = 0; R, R^1, R^2 =CH_3; R^3, R^4 = H:

4,4'-bis[2(4-methylphenylsulfonyl)-2-methyl-1-propanoyl]-diphenyl sulphide (Ia).

480 g of demineralizated water, 106.6 g of sodium bicarbonate and 82.2 g of sodium sulfite are loaded in a 1 liter flask. The mixture is heated at 75 °C and 132.2 g of p-toluensulfonylchloride are loaded in

30'.

At the end of the addition the mass is kept at 80 °C for 30', then it is cooled at 25 °C and filtered: 101 g of sodium p-toluensulfinate are thus recovered after drying. Then the preparation of the 4,4'-bis(2-bromo-2-methyl-1-propanoyl)-diphenyl sulfide is started:

200 g of methylene chloride, 46.6 g of diphenyl sulfide and 116.8 g of 2-bromoisobutyryl bromide are loaded in a 500 ml flask. In one hour, keeping the temperature between 0 °C and 10 °C, acting in an inert atmosphere. 70.0 g of aluminum trichloride are loaded.

At the end of the addition the mass is maintained under agitation for one hour at 15 °C. The solution so obtained is poured in a mixture of hydrochloric acid at 30% (15 g), ice (188 g) and methylene chloride (40 g), maintaining the temperature between 15 and 20 °C.

The two phases are separated, the aqueous phase is extracted with 40 g of solvent and the reunited organic phases are washed with 50 g of demineralizated water. The solvent is finally distilled, obtaining 117 g of 4,4'-bis(2-bromo-2-methyl-1-propanoyl)-diphenyl sulfide.

In the same reaction flask 365 g of n-butyl alcohol, 101 g of sodium p-toluensulfinate formerly prepared are added, and the whole is taken under reflux. It is left to reflux for 1 hour, it is cooled at 90 °C and a wash is done with demineralizated water (60 g).

Then the waters are removed and the solution is cooled. 138 g of 4,4'-bis[2(4-methylphenylsulfonyl)-2-methyl-1-propanoyl]diphenyl sulfide are thus obtained after filtration of the product.

^{1}H-NMR:	1.7 ppm (12H, s)	aliphatic	4 CH_3
	2.5 ppm (6H, s)	on aromatic	2 CH_3
	7.35-8.0 ppm (16H, m)	aromatic	16 H

IR Spectrum:	ν (cm^{-1})	Attribution
	1670	C=O
	1590	CH=CH
	1300-1320	SO_2
	1130-1150	SO_2

UV Spectrum (CH_2Cl_2: 5.66 mg/l): ϵmolar at 318 nm=23550

ϵmolar at 230 nm=49340

Melting point = 126 °C.

TLC (on silica, eluant: petroleum ether/ethyl acetate = 1/1): single spot at Rf = 0.43.

EXAMPLE 1 bis

Synthesis of the photoinitiator having formula (I) wherein n = 0; R, R^1 = CH_3, R^2 = CH_2-CH_3; R^3, R_4 = 0):

4,4'-bis[2(4-methylphenylsulfonyl)-2-methyl-1-butyryl]-diphenyl sulphide (Ib)

120 g of the above photoinitiator (Ib) are obtained by a process analogous to that followed in the example 1, by the use of 120 g of 2-bromo-2-methyl-butyryl bromide in alternative to 2-bromoisobutyrylbromide

^{1}H-NMR:	0.80 ppm	(6H, t)	aliphatic	$2\underline{CH_3}$-CH_2
	1.70 ppm	(6H, s)	aliphatic	$2\underline{CH_3}$-C
	2.48 ppm	(6H, s)	on aromatic	$2CH_3$
	2.40-2.54 ppm	(4H, m)	aliphatic	$2\underline{CH_2}$-CH_3
	7.29-7.88 ppm	(16H, m)	aromatic	16 H

IR Spectrum: $\bar{\nu}$ (cm^{-1})	Attribution
1660	C=O
1300	SO_2
1150	SO_2

UV Spectrum (CH_2Cl_2 : 40 mg/1): ϵmolar at 241 nm=24395

ϵmolar at 311 nm=19187

Melting point = about 60 °C

TLC (on silica, eluant: petroleum ether/ethylacetate = 1/1):

single spot at Rf = 0.84.

EXAMPLE 2

Synthesis of the photoinitiator having formula (II $R^1=R^2=CH_3$):

2,6 - bis [2(4-methylphenylsulfonyl)-2-methyl-1-propanoyl]-thianthrene (IIa).

140 g of the photoinitiator (IIa) are obtained by a process analogous to which followed in the example 1, using in spite of diphenyl sulfide 54 g of thianthrene.

^1H-NMR:	1.7 ppm (12H, s)	aliphatic	4 CH_3
	2.5 ppm (6H, s)	on aromatic	2 CH_3
	7.2-8.1 ppm (14H, m)	aromatic	14 H

IR Spectrum: $\bar{\nu}$ (cm^{-1})	Attribution
1670	C=O
1240-1310	SO_2
1150	SO_2

UV Spectrum (CH_2Cl_2; 10.2 mg/1): ϵmolar at 250 nm=35840

ϵmolar at 265 nm=29325

ϵmolar at 325 nm=5870

Melting point = 118 °C.

TLC (on silica, eluant: petroleum ether/ethyl acetate = 1/1):unitary spot at Rf = 0.51.

The substances used in the following examples are commercialized with the following commercial denominations:

Ebecryl 600®, UCB (Belgium): linear epoxyacrylate oligomer.

Ebecryl 220®, UCB (Belgium): aromatic urethanoacrylate oligomer.

Trimethylolpropanetriacrylate: base trifunctional monomer.

Irgalite Blue BNSF®, CIBA: blue pigment.

Efka Polymer LP 8001®, EFKA CHEMICALS BV: polyacrylic base dispersant.

Verol 368®, LAMBERTI SpA: sulfosuccinic base wetting agent.

Speedcure EDB®, LAMBSON LTD (UK): coinitiator. 4-dimethylamino-ethylbenzoate.

The comparison reported in the following examples has been carried out testing the following compounds:

- betaketosulfonic derivative (Ia);
- betaketosulfonic derivative (Ib);
- betaketosulfonic derivative (IIa);
- compound (III), corresponding to the 2-methyl-1-[4-(methylthio) phenyl] -2-(4-methylphenylsulfonyl) 1-propanone (contained in the American Patent US 5 026 740);
- compound (IV), corresponding to the 2-methyl-1-[4-(methylthyo)phenyl]-2-morpholino-1-propanone (contained in the European Patent EP 88050) (MMMP).

EXAMPLE 3

Composition of the matrix for the blue inks:

- reactive oligomers: (mixture of aromatic epoxy and urethanoacrylates).

Ebecryl 600® 43.0 %

Ebecryl 220® 11.5 %

- Reactive monomers:

Trimethylolpropane triacrylate 22.0 %

- Pigment:

Irgalite Blue BNSF® 22.0 %

- Additives:

Efka Polymer LP 8001® 0.6 %

Verol 368® 0.9 %

Composition of the cross-linkable blue inks:

		1	2	3	4	5
Matrix (%)		92	92	92	92	92
Compound (Ia)	(%)	4				
Compound (Ib)	(%)					4
Compound (IIa)	(%)		4			
Compound (III)	(%)			4		
Compound (IV)	(%)				4	
Speedcure EDB®	(%)	4	4	4	4	4

Preparation of the inks: the compositions are grinded on a three cilinders refiner till a granulometry lower than one micron and photocross-linked by irradiation in the above reported conditions.

EXAMPLE 4

Composition of the matrix for the white inks:

- reactive oligomers: (mixture of epoxy and urethanoaromatic acrylates).

Ebecryl 600® 26.6 %

Ebecryl 220® 7.1 %

- Reactive monomers:

Trimethylolpropane triacrylate 9.9 %

- Pigment:

Titanium dioxide (rutile) 55.5 %

- Additives:

Efka Polymer LP 8001® 0.35 %

Verol 368® 0.55 %

Composition of the cross-linkable white inks:

		6	7	8	9
Matrix (%)		95	95	95	95
Compound (Ia)	(%)	2.5			
Compound (IIa)	(%)		2.5		
Compound (III)	(%)			2.5	
Compound (IV)	(%)				2.5
Speedcure EDB®	(%)	2.5	2.5	2.5	2.5

Preparation of the inks: the compositions are grinded on a three cilinders refiner till a granulometry lower than one micron. and photocross-linked by irradiation in the above reported conditions.

The characterization of the so obtained inks is carried out analysing the following parameters:

Reactivity determination

The ink is applied at a thickness of 1 micron. by a mechanical coater equipped with head for offset applications. on a PVC support and then it is passed at a distance of 15 cm from the light source. under the

UV radiation of a 80 W/cm medium pressure mercury-vapor lamp, of which a Steinmann® photocross-linker is equipped. The greater is the line speed, the lower is the energy needed for the cross-linking, then the grater is the efficacy of the photoinitiator.

The cross-linking speed, measured in m/mim, is expressed as the maximum speed of the belt conveying the manufacture which allows the perfect ink cross-linking (tack free). The last is assured when, at the cross-linker outlet, the ink does not show superficial damagings after frictions with the edge of a folded sheet of paper or after repeated pressures and twists of the thumb well sticked on the surface (thumb twist test). In the above described conditions it is assumed that, if at the line velocity of 80 m/min the ink reaches the tack free conditions, it has a good applicative response.

DETERMINATION OF THE POST CURING ODOUR

The tested inks supported on PVC specimens, as above described for the reactivity determination, are passed under the indicated photocross-linker at a speed of 50 m/min to assure the complete polymerization and then the absence of odour due to the possible presence of unreacted acrylates, immediately ermetically and oven by one closed in jars and put in a thermostated oven at 60 °C. After 1 hour a group of 5 persons gives an opinion on the residual odour produced by the inked specimens signed in an anonymous way.

Then the persons give a qualitative opinion using a scale of empirical values between 1 and 5, where 1 means the minimum odour perception, and 5 means a strong perception.

DETERMINATION OF THE YELLOW INDEX

In order to measure the yellow index, the only PVC specimens on which

the white ink has been applied, immediately after the cross-linking, are put in the specimen holder of a BYK® colorimeter and the yellow index is measured according to the ASTM E 313 specification.

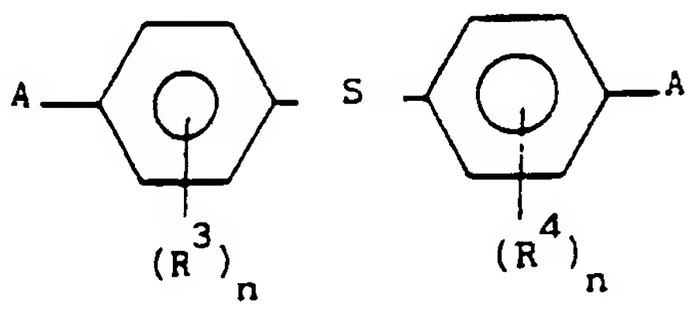
RESULTS

Blue Inks	1	2	3	4	5
Cross-linking velocity (m/min)	>80	>80	>80	>80	>80
Post curing residual odour (average)	1	2-3	3-4	5	1
White Inks	6	7	8	9	
Cross-linking velocity (m/min)	>65	>65	>65	>65	
Post curing residual odour (average)	1	2-3	3-4	5	
Yellow Index	7.5	7.7	7.6	7.5	

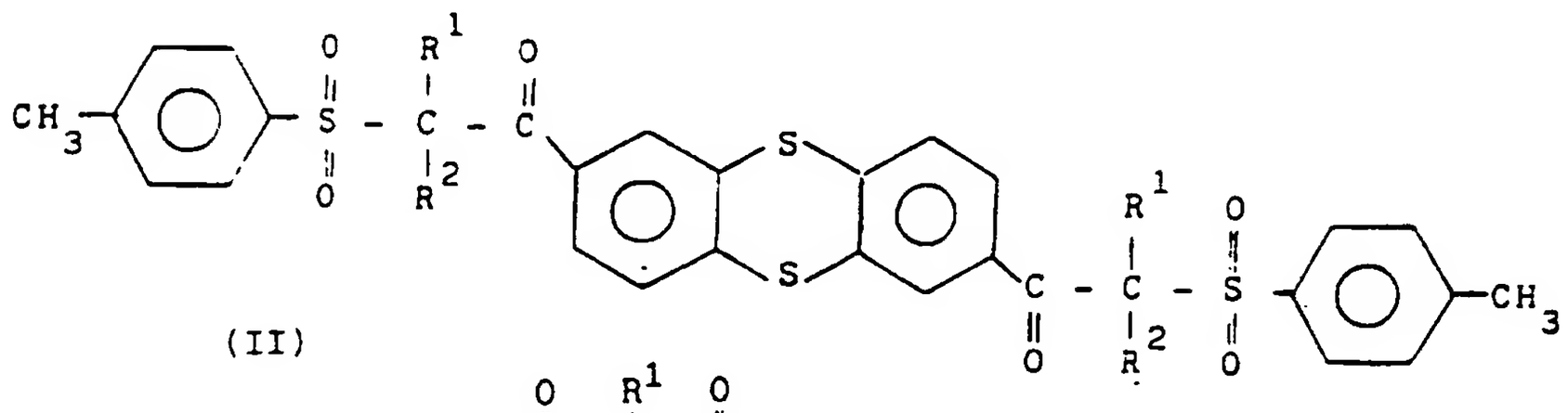
As it is possible to notice from the just reported data, the presence of the betaketosulfonic derivatives (I) and (II) in the tested inks, in addition to assuring good applicative characteristics in terms either of line velocity or of yellow index, has the merit to give a scarce residual odour.

CLAIMS

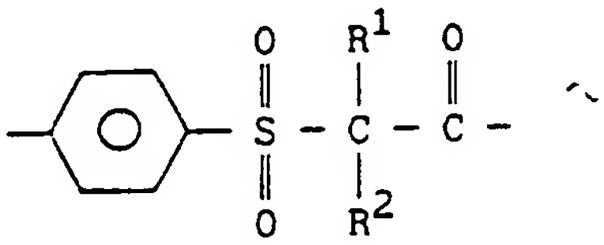
1. Photopolymerizable system containing at least a betaketosulfonic derivative selected from the compounds having formuia (I) and (II):



(I)



(II)

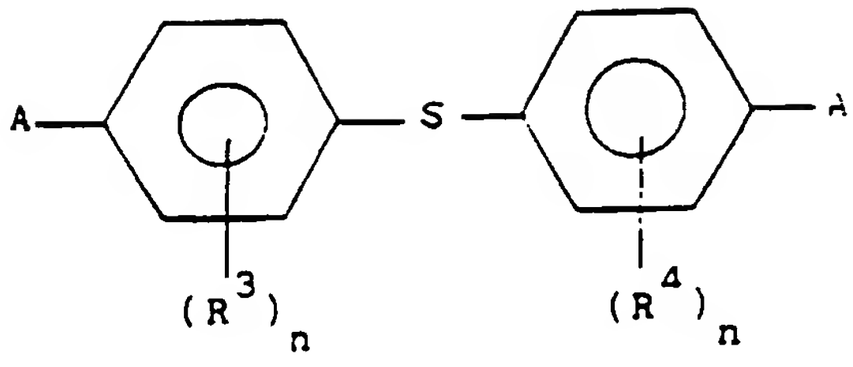
wherein A is R 

and R, R^1, R^2, R^3 and R^4 each independently are H or C_{1-4} linear or branched alkyl chain and n is 0 or 1

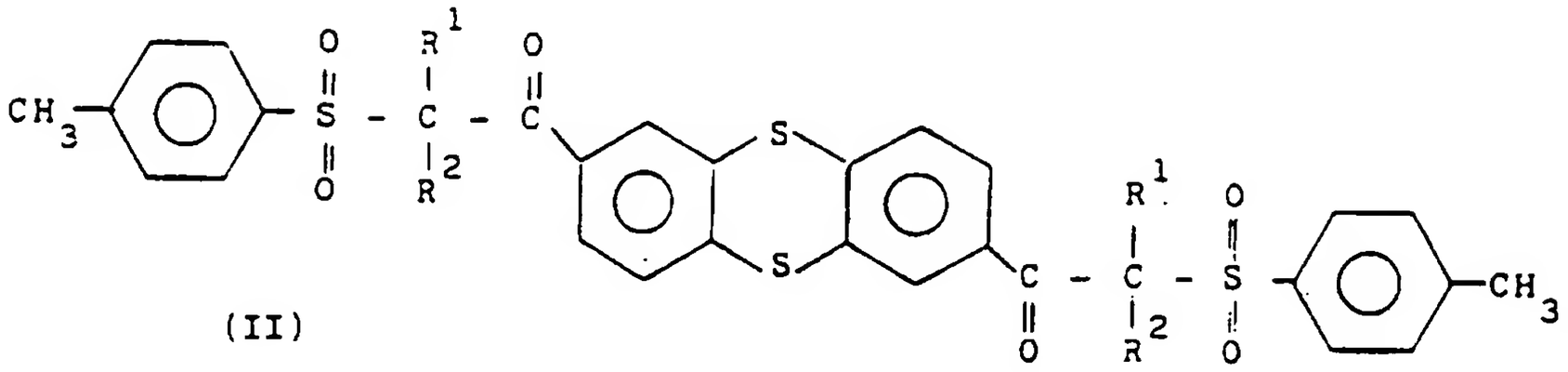
in an amount ranging from 0.01 to 20 % by weight.

2. Photopolymerizable system as claimed in claim 1, wherein said betaketosulfonic derivative is contained in an amount ranging from 0.5 and 5 % by weight.

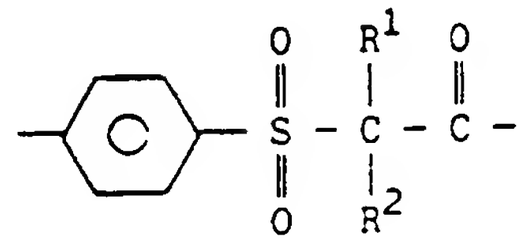
3. Pigmented ink containing at least a betaketosulfonic derivative selected from the compounds having formula (I) and (II):



(I)



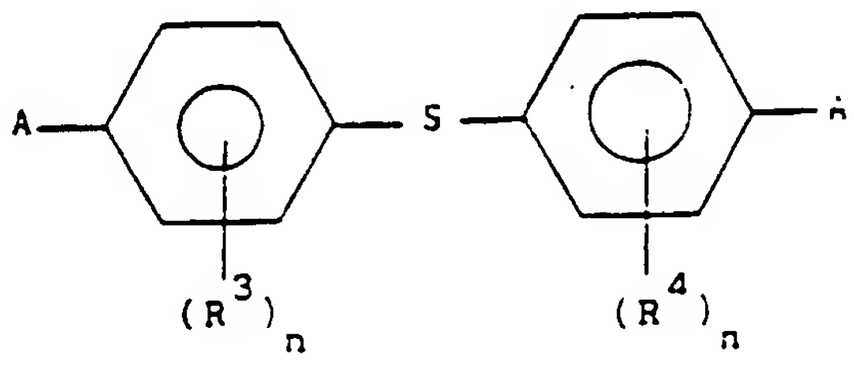
(II)

wherein A is R 

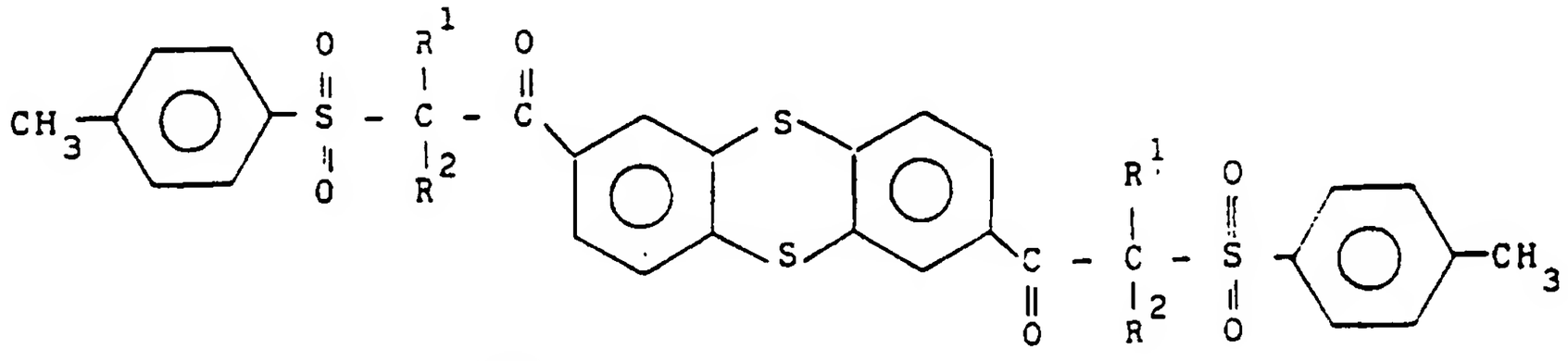
and R, R^1, R^2, R^3 and R^4 each independently are H or C_{1-4} linear or branched alkyl chain and n is 0 or 1

in an amount ranging from 0.01 to 20 % by weight.

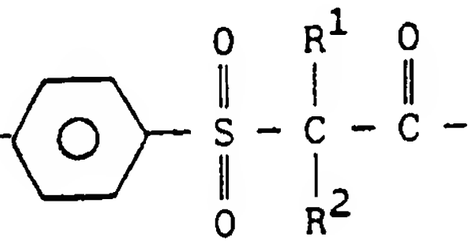
4. Betaketosulfonic derivative selected from the group consisting of (I) and (II):



(I)



(II)

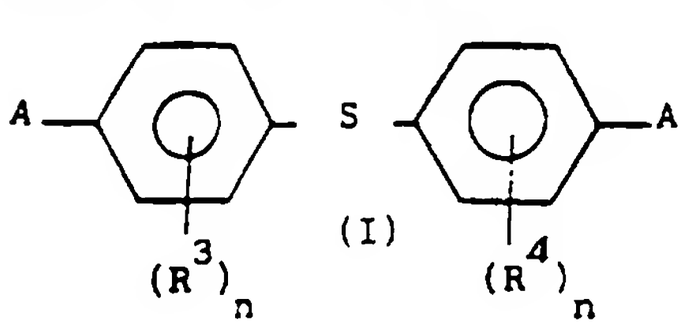
wherein A is R 

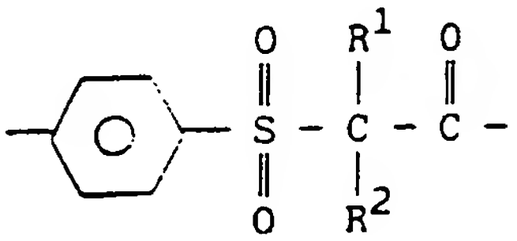
and R, R^1, R^2, R^3 and R^4 each independently are H or C_{1-4} linear or branched alkyl chain and n is 0 or 1

suitable to the use as polymerization photoinitiator.

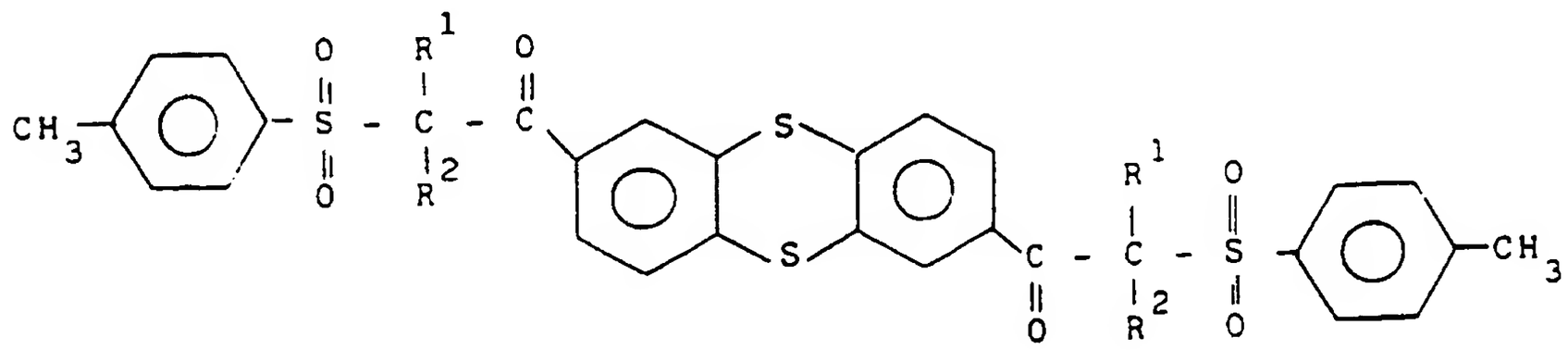
5. Use of at least one betaketosulfonic derivative selected from the group consisting of (I) and (II) as claimed in claim 4, as polymerization photoinitiator for inks having high content in pigments.

6. Process for the preparation of a betaketosulfonic derivative selected from the group consisting of (I)



wherein A is R 

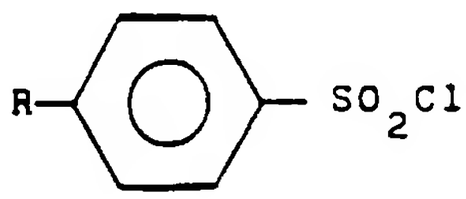
and II



wherein

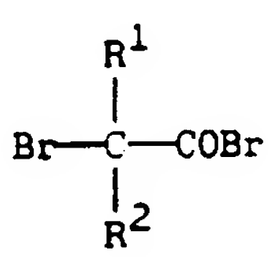
R, R^1, R^2, R^3, R^4 each independently are H or C_{1-4} linear or branched alkyl chain and n is 0 or 1 comprising the following reaction steps:

a) a mixture of arylsulfonyl chloride of formula (III), sodium bicarbonate and sodium sulfite in a polar solvent, is made to react, obtaining the sodium arylsulfinate;

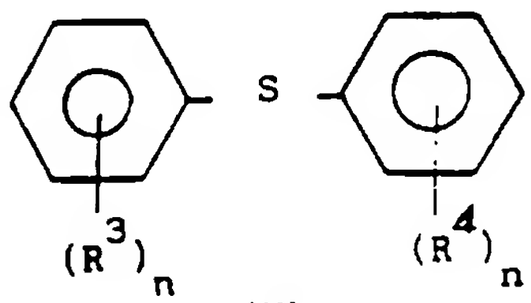


(III)

b) the dialkylbromoacetyl bromide of formula (IV) is made to react with the diphenyl sulfide of formula (V) or with thianthrene, in presence of aluminum trichloride, in an organic solvent, and the mixture is neutralized with mineral acids to give the corresponding 2-bromoketones;



(IV)



(V)

c) a mixture of sodium arylsulfinate obtained in the step a) and the 2-bromoketone obtained by the step b), in an organic solvent is heated to give the final products (I) or (II).

INTERNATIONAL SEARCH REPORT

Interr al Application No
PCT/EP 95/03567

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/50 G03F7/031 C07C323/65

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F G03F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 192 967 (F.LAMBERTI S.P.A.) 3 September 1986 see claim 1 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 June 1996	12. 06. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Cauwenberg, C

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter al Application No
PCT/EP 95/03567

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-192967	03-09-86	CH-A-	672316	15-11-89
		JP-A-	63030503	09-02-88
		US-A-	5026740	25-06-91